Efficient Large-Scale Synthesis of Picolinic Acid-Derived Nickel(II) Complexes of Glycine

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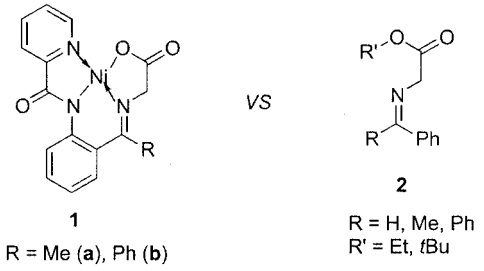
An efficient, large-scale method for the preparation of 2-[*N*-(α-picolyl)amino]acetophenone (PAAP) and 2-[*N*-(α-picolyl)-amino]benzophenone (PABP), the hitherto unknown 4-methyl-2-[*N*-(α-picolyl)amino]benzophenone (4-Me-PABP) and 4-nitro-2-[*N*-(α-picolyl)amino]benzophenone (4-NO_2-PABP), and their corresponding Ni^{II} complexes with glycine is described. The key step of the method is the formation of the mixed anhydrides derived from *o*-picolinic acid and ethyl chloroformate or *p*-toluenesulfonyl chloride.

Picolinic acid-derived (PA-derived) Ni^{II} complexes **1a** and **1b** (Scheme 1) have emerged as a new type of highly efficient achiral nucleophilic glycine equivalents.[1−3] Their superior qualities in relation to conventional *N*-(phenylmethylene)glycine derivatives **2** include chemical stability and predictable formation of the corresponding (*Z*) geometrically homogeneous enolates,[4] a feature of paramount importance for highly enantioselective homologation of the glycine moieties in **1a** and **1b**. Thus, we and others have demonstrated an efficient application of complexes **1a** and **1b** as glycine equivalents in asymmetric Michael addition reactions[1] and catalytic alkylations under phase-transfer conditions.[2] Moreover, we recently reported an efficient synthesis of symmetrically *bis*-substituted amino acids by use of complex **1b** as a stable yet highly reactive glycine equivalent under the strongly basic reaction conditions.[3]



1
R = Me (**a**), Ph (**b**)

2
R = H, Me, Ph
R' = Et, *t*Bu

Scheme 1

Previously, we had reported the synthesis (95% yield) of 2-[*N*-(α-picolyl)amino]acetophenone (PAAP, **3a**; Scheme 2), the ligand for complex **1a**, starting from PA and 2-aminoacetophenone and with the use of BOP (benzotriazol-1-yloxy-tris(dimethylamino)phosphonium hexafluorophosphate) as condensing reagent.[4] On the other hand, 2-[*N*-(α-picolyl)amino]benzophenone (PABP, **3b**), the ligand for complex **1b**, was prepared in 85% yield from 2-aminobenzophenone and thionyl chloride through the in situ formation of the corresponding chloroanhydride of PA.[2] For systematic studies of complexes **1a** and **1b**, and in particular their application as nucleophilic glycine equivalents for asymmetric synthesis of amino acids, our group needed an expeditious and reliable method for large-scale preparation of **1a** and **1b**. We found that the literature methods,[2,4] though successful, are unattractive for this purpose. For instance, the synthesis of **3a** and **3b** by application of peptide coupling reagents such as BOP is a very simple and convenient approach and could be effectively used for relatively small-scale preparations. For large-scale synthesis, however, the high molecular weights and cost of these reagents render this method economically unattractive. On the other hand, application of cheap thionyl chloride has serious synthetic disadvantages, such as substantial formation of by-products, necessitating laborious purification of ligands **3a** and **3b**. In this paper we describe a simple and efficient method for the large-scale preparation of ligands **3a** and **3b**, as well as their hitherto unknown derivatives 4-methyl-2-[*N*-(α-picolyl)amino]benzophenone (4-Me-PABP) **3c**, 4-nitro-2-[*N*-(α-picolyl)amino]benzophenone (4-NO_2-PABP) **3d**, and their corresponding Ni^{II} complexes with glycine **1a**−**d**.

Amidation of carboxylic acids in general and formation of a peptide bond in particular has been an area of intense research and is well documented.[5] The reagents most commonly used to increase the electrophilicity of the carboxylic function are carbodiimides,[6] 1,1′-(carbonyldioxy)dibenzotriazole,[7] sulfuryl chloride fluoride,[8] arylsulfonyl chlorides,[9] alkyl chloroformates,[10] and others.[11] Unfortu-

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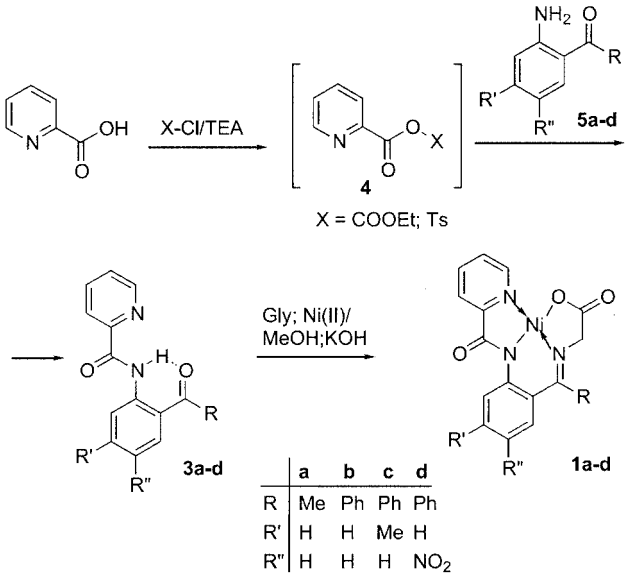

Scheme 2

nately, in all these publications the synthetic power and generality of the methods is demonstrated by the use of an admittedly wide range of amines, but only of conventional ones, rarely including examples possessing a sterically hindered or weakly nucleophilic amino function. Therefore, amidation of acids with *o*-aminoaceto- and -benzophenone derivatives **5a**–**d** is a rather challenging task, as these compounds possess the undesirable features both of steric constraint and of low amino group nucleophilicity. Of the methods cited above, activation of the carboxylic function by in situ formation of the corresponding mixed carboxylic-sulfonic or -carbonic anhydrides was shown to be the most effective for reactions with sterically hindered or weakly nucleophilic amines.[9,10] We first tried the amidation of PA with acetophenone **5a** by use of ethyl chloroformate and triethylamine (TEA) to form the intermediate anhydride **4** (X = COOEt) (Scheme 2). Unfortunately, the reaction proceeded sluggishly, giving rise to a mixture of the target product **3a** and the starting amine **5a** in a ratio of 66/34 (Table 1, Entry 1). Under the same reaction conditions, we treated PA with *p*- and *m*-aminoacetophenones, and this afforded the corresponding products in high chemical yields (Entries 2 and 3). These results clearly suggested that electron-withdrawing and shielding effects (more pronounced) of the acyl group in **5a** do indeed have detrimental consequences on its reactivity. We next decided to use *p*-toluenesulfonyl chloride instead of ethyl chloroformate, since the *p*-tosyloxy group generally exhibits superior leaving ability. The result was fairly satisfactory, as we observed up to 89% conversion of the starting amine **5a** (Entry 4). Complete conversion was achieved when we used 1.2 equiv. of the intermediate anhydride (Entry 5). Without any additional purification, compound **3a** was used to prepare the corresponding Ni^{II} complex **1a** under reaction conditions described previously.[2] To demonstrate the reliability and efficiency of this procedure, the preparation of ligand **3a** and its Ni^{II} complex **1a** was repeated on > 100 g scale with > 93% overall yield.

With these results in hand we turned our attention to the amidation of PA with *o*-aminobenzophenone derivatives **5b**–**d**. We first conducted a reaction between PA and amine **5b** under the conditions that we had found to give the best result for the amidation with **5a**. The reaction proceeded at a substantially faster rate, affording the target compound **3d** in quantitative chemical yield (Entry 6). Taking advantage of the higher reactivity of *o*-aminobenzophenone **5b**, we performed the amidation with ethyl chloroformate instead of *p*-toluenesulfonyl chloride. The reaction proceeded smoothly, affording virtually complete chemical conversion, as was also observed with the more reactive *p*-toluenesulfonyl chloride (Entry 6 vs. 7). This procedure, using ethyl chloroformate, was also successfully reproduced on a

Table 1. Amidation of Picolinic Acid with Amines **5a**–**d** via Intermediate Mixed Anhydrides **4**

Entry[a]	Amine **5a**–**d**	X in **4**	Ratio **5a**–**d**/**3a**–**d**[b]	Yield[c] of **3a**–**d** (%)
1	**a**	COOEt	34/66	N.D.
2	–[d]	COOEt	4/96	92
3	–[e]	COOEt	>1/99	98
4	a	Ts	11/89	>85
5	a	Ts[f]	>1/99	>94
6	b	Ts[f] [g]	>1/99	99
7	b	COOEt[f]	>1/99	99
8	c	Ts[f]	>1/99	99
9	c	COOEt	7/93	91
10	c	COOEt[f]	>1/99	97
11	d	Ts	46/54	N.D.
12	d	COOEt	49/51	N.D.
13	d	Ts[h]	20/80	78
14	d	Ts[h] [i]	>1/99	99

[a] All reactions were run in commercial grade DCM overnight in the presence of TEA (PA/**5** = 1.1/1). [b] Determined by NMR (300 MHz) analysis of the crude reaction mixtures. [c] Isolated yield of pure products based on **5**. [d] *p*-Aminoacetophenone was used in place of **5a**. [e] *m*-Aminoacetophenone was used in place of **5a**. [f] PA/**5** = 1.2/1. [g] Reaction time was 4 h. [h] Reaction was conducted in the presence of DMAP. [i] Reaction was conducted in dichloroethane.

>100 g scale, thus proving its efficiency and practicality. Under the same reaction conditions, 4-methyl-substituted amine **5c** was used to prepare the new ligand **3c** with a virtually complete chemical conversion both with *p*-toluenesulfonyl chloride (Entry 8) and with ethyl chloroformate (Entry 9, 10). In contrast, application of our standard conditions for preparation of ligand **3d** starting from the NO_2-containing amine **5d** gave unsatisfactory results (Entries 11, 12). To improve these results we decided to use 4-(dimethylamino)pyridine (DMAP) as a catalyst, as it has a known powerful effect on many reactions, including acylations on nitrogen.[12] After several attempts we found that the application of DMAP in stoichiometric amounts could have a noticeable effect on the chemical outcome (Entry 13). To improve the results further we conducted the amidation in dichloroethane, allowing us to run the reaction at a higher temperature and to obtain the target compound in quantitative chemical yield (Entry 14).

The corresponding Ni^{II} complexes **1a**−**d** were prepared from ligands **3a**−**d** in high chemical yields under previously reported conditions.[2] In the ^1H NMR spectra of complexes **1b**−**d**, the protons of the glycine methylene moiety were found to be sensitive to the effect of the substituent. Thus, the chemical shift of the glycine methylene group protons in **1d** was found to be shifted downfield (δ = 3.88 ppm) and in **1c** shifted upfield (δ = 3.79 ppm), relative to that of the unsubstituted complex **1b** (δ = 3.83 ppm). This data suggested that the glycine methylene moiety in **1d** is more, and in **1c** less, CH acidic than the known complex **1b**. This observation provides grounds for a rational design of this type of complexes with controlled reactivity of the glycine methylene group.

In summary, an efficient, large-scale method for the preparation of PAAP and PABP, the hitherto unknown ligands 4-Me-PABP and 4-NO_2-PABP, and their corresponding Ni^{II} complexes with glycine has been developed. The key step of the method is the formation of the mixed anhydrides derived from *o*-picolinic acid and ethyl chloroformate or *p*-toluenesulfonyl chloride. The synthetic efficiency and practicality of the methods were demonstrated by the preparation of the target Ni^{II} complexes on >100 g scales.

Experimental Section

General: ^1H and ^{13}C NMR (299.94 MHz) were recorded with TMS, $CDCl_3$, and CCl_3F as internal standards. High-resolution mass spectra (HRMS) were recorded on facilities at the Department of Chemistry, University of Oklahoma. Melting points (m.p.) are uncorrected and were obtained in open capillaries. All reagents and solvents, unless otherwise stated, are commercially available and were used as received. Unless otherwise stated, yields refer to isolated yields of products of greater than 95% purity as estimated by ^1H and ^{13}C NMR spectrometry. All new compounds were characterized by ^1H and ^{13}C NMR and HRMS. Abbreviations used in the paper: PA: picolinic acid, BOP: benzotriazol-1-yloxy(dimethylamino)phosphonium hexafluorophosphate, TEA: triethylamine, DCM: dichloromethane, DMAP: 4-(dimethylamino)pyridine.

Large-Scale Preparation of Ligand 3b by the Use of ClCOOEt; Typical Procedure: Ethyl chloroformate (87.48 g, 0.81 mol) was added at 0 °C under N_2 to a flask containing picolinic acid (99.65 g, 0.81 mol), triethylamine (81.91 g, 0.81 mol), and CH_2Cl_2 (1.36 L). After the mixture had been stirred at room temperature for 20 min, **5b** (134.02 g, 0.68 mol) was added and the mixture was kept stirring at 40−50 °C overnight. Water was then added to quench the reaction, and the organic phase was washed three times with water. After evaporation of the CH_2Cl_2, washing of the crude precipitate with ether afforded the target product **3b** (200.73 g, 97.61%), which were used for preparing the corresponding Ni^{II} complex **1b** without further purification.

This procedure was successfully reproduced for the preparation of ligand **3c**.

Large-Scale Preparation of Ligand 3a by Use of TsCl: TsCl (45.60 g, 0.24 mol) and **5a** (27.02 g, 0.20 mol) were added, in that order, at 0 °C under N_2 to a flask containing picolinic acid (29.53 g, 0.24 mol), triethylamine (40.45 g, 0.40 mol), and CH_2Cl_2 (200 mL), and the mixture was stirred at 40−50 °C overnight. AcOH (5% aq.) was then added to quench the reaction, and the organic phase was washed three times with water. After evaporation of the CH_2Cl_2, washing of the crude precipitate with ether furnished the desired ligand **3a** (46.51 g, 96.84%), which was used without further purification for preparation of the corresponding Ni^{II} complex **1a**.

This procedure was successfully reproduced for the preparation of ligand **3c**.

Preparation of Ligand 3d: Triethylamine (5.41 mL, 38.50 mmol), DMAP (4.28 g, 35.06 mmol), $ClCH_2CH_2Cl$ (100 mL), TsCl (7.34 g, 38.63 mmol), and 2-amino-5-nitrobenzophenone (8.48 g, 35.03 mmol) were added in that order at 0 °C under N_2 to a flask containing picolinic acid (4.74 g, 38.53 mmol). The mixture was then heated at 60−70 °C and stirred overnight. The reaction was quenched by addition of aq. AcOH (5%) and the organic phase was washed three times with water. After evaporation of the CH_2Cl_2, washing of the crude precipitate with EtOAc afforded the desired product **3d** (12.43 g, 98.95% yield), which was used without further purification for preparation of the corresponding Ni^{II} complex **1d**.

2-(Picolinoylamino)acetophenone (PAAP, 3a):[4] M.p. 112.4 °C. ^1H NMR ($CDCl_3$): δ = 2.73 (s, 3 H), 7.16−7.21 (m, 1 H), 7.47−7.51 (m, 1 H), 7.60−7.66 (m, 1 H), 7.90 (dt, *J* = 8.7 Hz, 1.7 Hz, 1 H), 7.97 (dd, *J* = 7.8 Hz, 1.5 Hz, 1 H), 8.29 (d, *J* = 8.1 Hz, 1 H), 8.80−8.82 (m, 1 H), 9.03 (dd, *J* = 8.5 Hz, 1.0 Hz, 1 H), 13.5 (br. s, 1 H) ppm.

3-(Picolinoylamino)acetophenone: M.p. 78.5 °C. ^1H NMR ($CDCl_3$): δ = 2.64 (s, 3 H), 7.48 (t, *J* = 7.69 Hz, 1 H), 7.50 (ddd, *J* = 7.57, 4.76, 1.22 Hz, 1 H), 7.73 (ddd, *J* = 7.82, 1.71, 1.10 Hz, 1 H), 7.92 (td, *J* = 7.82, 1.71 Hz, 1 H), 8.08 (ddd, *J* = 7.05, 2.19, 1.10 Hz, 1 H), 8.28 (ddd, *J* = 7.81, 1.10, 0.98 Hz, 1 H), 8.32 (dd, *J* = 2.07, 1.71 Hz, 1 H), 8.61 (ddd, *J* = 4.76, 1.71, 0.85 Hz, 1 H), 10.2 (br. s, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 26.8, 119.1, 122.2, 123.8, 123.9, 126.5, 129.2, 137.5, 137.6, 138.0, 147.8, 149.1, 162.0, 197.5 ppm. HRMS [M + Na^+] found *m/z* 263.0713, calcd. for $C_{14}H_{12}N_2NaO_2$ 263.0796.

4-(Picolinoylamino)acetophenone: M.p. 173.2 °C. ^1H NMR ($CDCl_3$): δ = 2.60 (s, 3 H), 7.51 (ddd, *J* = 6.556, 4.76, 1.22 Hz, 1 H), 7.76−8.04 (m, 5 H), 8.30 (ddd, *J* = 7.81, 1.22, 0.98 Hz, 1 H), 8.62 (ddd, *J* = 4.76, 1.71, 0.97 Hz, 1 H), 10.2 (br. s, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 26.6, 118.8, 122.4, 126.7, 129.7, 132.7, 137.6,

141.8, 147.8, 149.0, 162.0, 196.6 ppm. HRMS [M + Na^+] found *m/z* 263.0981, calcd. for $C_{14}H_{12}N_2NaO_2$ 263.0796.

2-(Picolinoylamino)benzophenone (PABP) (3b):[2] M.p. 154.9 °C. ^{1}H NMR ($CDCl_3$): δ = 7.07 (m, 1 H), 7.35−7.43 (m, 3 H), 7.43−7.60 (m, 3 H), 7.65−7.71 (m, 2 H), 7.81 (td, *J* = 7.69, 1.71 Hz, 1 H), 8.21 (br. d, *J* = 7.82 Hz, 1 H), 8.68 (ddd, *J* = 4.76, 1.71, 0.85 Hz, 1 H), 8.82 (d, *J* = 8.30 Hz, 1 H), 12.6 (br. s, 1 H) ppm.

4-Methyl-2-(picolinoylamino)benzophenone (4-Me-PABP) (3c): M.p. 182.9 °C. ^{1}H NMR ($CDCl_3$): δ = 2.47 (s, 3 H), 6.94 (dq, *J* = 4.88, 0.86 Hz, 1 H), 7.40−7.60 (m, 5 H), 7.70−7.80 (m, 2 H), 7.88 (td, *J* = 7.82, 1.71 Hz, 1 H), 8.28 (d, *J* = 7.81 Hz, 1 H), 8.72−8.86 (m, 2 H), 12.9 (br. s, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 22.3, 121.8, 121.9, 122.4, 123.1, 126.2, 128.0, 129.7, 131.9, 133.7, 137.2, 138.9, 139.9, 145.1, 148.5, 150.0, 163.4, 198.6 ppm. HRMS [M + Na^+] found *m/s* 339.1007, calcd. for $C_{20}H_{16}N_2NaO_2$ 339.1010.

5-Nitro-2-(picolinoylamino)benzophenone (5-NO_2-PABP) (3d): M.p. 236.4 °C. ^{1}H NMR ($CDCl_3$): δ = 7.48 (m, 3 H), 7.62−7.70 (m, 1 H), 7.76−7.86 (m, 2 H), 7.93 (td, *J* = 7.81, 1.71 Hz, 1 H), 8.30 (ddd, *J* = 7.81, 1.22, 0.86 Hz, 1 H), 8.45−8.52 (m, 2 H), 8.78 (dd, *J* = 0.86, 1.59 Hz, 1 H), 9.17 (d, *J* = 9.28 Hz, 1 H), 13.0 (br. s, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 121.2, 122.7, 123.8, 126.8, 128.3, 128.4, 128.5, 129.7, 137.1, 137.1, 137.3, 141.2, 144.8, 148.5, 148.8, 163.5, 196.7 ppm. HRMS [M + Na^+] found *m/s* 370.0924, calcd. for $C_{19}H_{13}N_3NaO_4$ 370.0804.

For preparation of the Ni^{II} complexes **1a**−**d** described previously, the general procedure[4] was followed.

Ni^{II} Complex of Glycine Schiff Base with PAAP (1a):[4] Yield 97.35%. M.p. > 290 °C (dec.). ^{1}H NMR ($CDCl_3$): δ = 2.43 (s, 3 H), 4.20 (s, 2 H), 7.01 (m, 1 H), 7.32−7.43 (m, 2 H), 7.63 (d, *J* = 8.55 Hz, 1 H), 7.81 (d, *J* = 7.33 Hz, 1 H), 7.95 (t, *J* = 7.57 Hz, 1 H), 8.18 (d, *J* = 4.88 Hz, 1 H), 8.69 (d, *J* = 8.79 Hz, 1 H) ppm.

Ni^{II} Complex of Glycine Schiff Base with PABP (1b):[2] Yield 99.07%. M.p. > 270 °C (decomp). ^{1}H NMR ($CDCl_3$): δ = 3.83 (s, 2 H), 6.83 (br. t, *J* = 7.57 Hz, 1 H), 6.91 (br. d, *J* = 7.81 Hz, 1 H), 7.11 (br. d, *J* = 7.08 Hz, 2 H), 7.34−7.47 (m, 2 H), 7.50−7.60 (m, 2 H), 7.89 (br. d, *J* = 6.83 Hz, 1 H), 7.99 (m, 1 H), 8.29 (br. d, *J* = 5.37 Hz, 1 H), 8.99 (d, *J* = 8.06 Hz, 1 H) ppm.

Ni^{II} Complex of Glycine Schiff Base with 4-Me-PABP (1c): Yield 92.78%. M.p. > 270 °C (dec.). ^{1}H NMR ($CDCl_3$): δ = 2.33 (s, 3 H), 3.79 (s, 2 H), 6.61 (m, 1 H), 6.78 (d, *J* = 8.31 Hz, 1 H), 7.09 (m, 2 H), 7.43 (ddd, 1 H, *J* = 7.08 Hz), 7.48−7.60 (m, 3 H), 7.87 (m, 1 H), 7.98 (td, *J* = 7.56, 1.22 Hz, 1 H), 8.26 (m, 1 H), 8.85 (br. s, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 61.7, 122.7, 123.3, 123.8, 124.2, 125.9, 126.8, 129.4, 134.3, 134.6, 140.3, 142.8, 144.4, 146.7, 153.2, 170.2, 172.4, 177.2 ppm. HRMS [M + Na^+] found *m/z* 452.0668, calcd. for $C_{22}H_{17}N_3NaNiO_3$ 452.0521.

Ni^{II} Complex of Glycine Schiff Base with 5-NO_2-PABP (1d): Yield 95.43%. M.p. > 300 °C (dec.). ^{1}H NMR ($CDCl_3$): δ = 3.88 (s, 2 H), 7.00−7.38 (m, 4 H), 7.54 (m, 1 H), 7.62 (m, 1 H), 7.85 (d, *J* = 2.44 Hz, 1 H), 7.95 (d, *J* = 7.81 Hz, 1 H), 8.06 (dd, *J* = 7.69, 7.57 Hz, 1 H), 8.16 (dd, *J* = 9.28, 2.20 Hz, 1 H), 8.34 (d, *J* = 4.89 Hz, 1 H), 9.13 (d, *J* = 9.64 Hz, 1 H) ppm. HRMS [M + H^+Na^+] found *m/z* 485.0386, calcd. for $C_{21}H_{15}N_4NaNiO_5$ 485.0509. calcd. for $C_{21}H_{14}N_4NiO_5$ 461.05, C, 54.71, H 3.06, N 12.15; found C 54.88, H 3.16, N 12.11.

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